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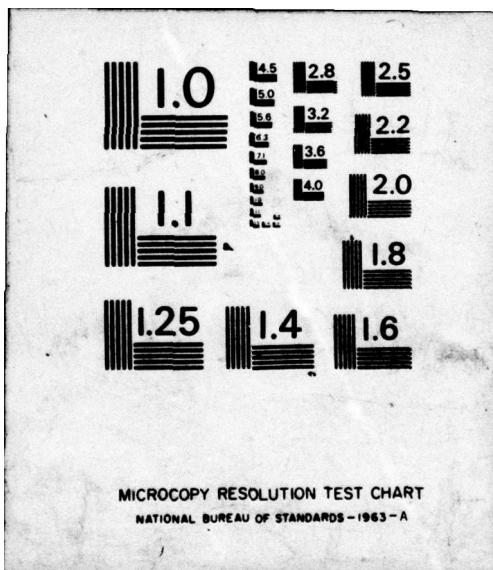
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Project No. NR 356-604

TECHNICAL REPORT NO. 1

ATTEMPTED PREPARATION OF POLYORGANONITRILES

by

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**Horizons Research Incorporated
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December 1976

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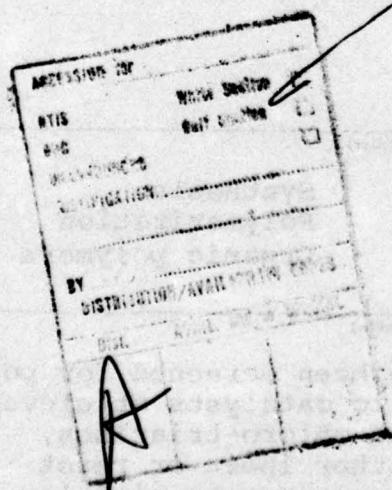
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20. Abstract (continued)

to give low molecular weight products with extensive loss of volatile materials which are thought to be fluorine containing materials. Preparation of the potential monomer trifluoroethyl cyanate has led to simultaneous formation of nonvolatile product which may contain polymeric material.



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ABSTRACT

A variety of triazine monomers have been screened for polymerizability using metallic and nonmetallic catalysts at elevated temperatures. Cyanuric chloride, bromo-chloro-triazines, 2,4-dichloro-6-phenyl-triazine, are either inert or react slowly with or without chemical side reactions to give low molecular weight products. The novel monomers mono- and bis-(trifluoroethoxy)-chloro-triazines react degradatively to give low molecular weight products with extensive loss of volatile materials which are thought to be fluorine containing materials. Preparation of the potential monomer trifluoroethyl cyanate has led to simultaneous formation of nonvolatile product which may contain polymeric material.

ATTEMPTED PREPARATION OF POLYORGANONITRILES

1.0 INTRODUCTION AND BACKGROUND

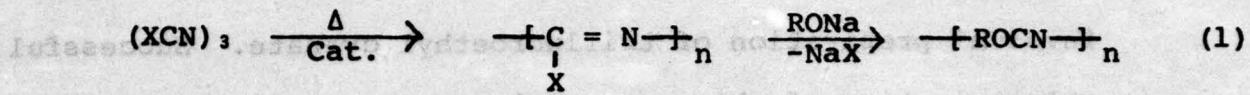
Polyorganonitriles are of interest because they are potentially relatively inexpensive, should display excellent thermal and chemical resistance, and could be prepared via a two-step synthesis from available starting materials.

Cyanuric chloride sells for less than one dollar a pound and is extraordinarily stable when heated in dry air. The $(\text{ClCN})_n$, and its aryloxy and aryl derivatives likewise are thermally stable. Many of these triazines melt well above 230°C without decomposition [Ref. 1] and, in fact, 2,4,6-triphenyl-s-triazine is claimed to be stable to distillation in excess of 350°C (662°F) at one atmosphere pressure.

The preparation and characterization of linear poly-nitriles has been very limited to date. Preparation of soluble high molecular weight specie has not been disclosed. The prior art for the preparation of $(\text{ClCN})_n$ polymer and of the derivatives is small and somewhat unspecific. Preparative approaches often involved the use of catalyzed high temperature reactions or ionizing radiation. The materials obtained were incompletely characterized and molecular weights when reported were low. For example, cyanuric chloride was polymerized at temperatures of at least 300°C in the presence

of catalyst [Ref. 2] or with Co^{60} radiation in the solid state [Refs. 3,4]. When the radiation polymerization was conducted under high vacuum, low molecular weight polymer (intrinsic viscosity of 0.2 in DMF) which melted above 260°C was obtained [Ref. 3]. The preparation of polynitriles $(\text{ROCN})_n$ ($\text{R}=\text{alkyl, phenyl}$) and of polybenzonitrile $(\text{C}_6\text{H}_5\text{CN})_n$ from the appropriate 2,4,6-trisubstituted-s-triazine or benzonitrile required temperatures of at least 300°C , often in the presence of catalyst [Refs. 5, 6, 7]. Polybenzonitrile of very low molecular weight (1250), unspecified linearity and high melting point ($>340^\circ\text{C}$) was formed at ambient temperatures by Co^{60} irradiation of a dilute (0.1-1.5%) aqueous solution of benzonitrile [Ref. 8]. Polybenzonitrile was reported not to degrade upon alkaline fusion and only slightly degraded when heated at 240°C (464°F) for 200 hours in the presence of 30% sulfuric acid [Ref. 9]. Lastly, synthesis of polyalkyl or polyarylnitriles has been accomplished by acid rearrangement of the relatively unavailable polyisocyanides $[-\text{C}(\text{:NR})\text{C}(\text{:NR})-]_n$ [Ref. 10].

The major approach investigated for the preparation of polyorganonitriles under Contract No. N00014-75-C-0991 during the period January-October 1976 involved a ring opening polymerization of a halotriazine with subsequent ligand exchange of reactive halogens as shown in Equation (1):



where X equals Cl, Br, and 1-2 halogen atoms in monomer may be replaced by a monovalent organic radical R

This synthetic scheme is analogous to one used for the preparation of poly(organophosphazenes) (phosphorus-nitrogen polymers) of structure $[(RO)(R'O)PN]_n$ (where R may be identical to R') from the cyclic monomer $(Cl_2PN)_3$. Horizons has conducted successful work on poly(organophosphazenes) for many years and this work has included fundamental polymerization studies, extensive synthesis, characterization, compounding and crosslinking, and determination of physico-mechanical properties of the vulcanizates [Refs. 11-17]. Dependent on the R and R' substituents a wide variety of plastics and elastomers can be prepared which have varying degrees of chemical, fuel and fire resistance, and ability to crosslink. The tailoring of physical and chemical properties by simple structure changes in poly(organophosphazenes) has been demonstrated. All this experience is expected to transfer over to poly-organonitriles technology. Thus an infinite variety of polymers should be derivable from $(ClCN)_n$ polymer or derivatives thereof.

An alternate approach, which received low priority, involved preparation of trifluoroethyl cyanate. Successful polymerization of this potential monomer would afford the polyorganonitrile $\text{---}[\text{C} = \text{N}]\text{---}_n$. Copolymerization with other OCH_2CF_3 , $\text{R}_f\text{CH}_2\text{OC}\equiv\text{N}$ monomers could produce elastomeric polymers. Analogously, many poly(fluoroalkoxyphosphazene) copolymers are elastomeric [Refs. 11, 12, 14, 15].

2.0 OBJECTIVES

Preparation of high molecular weight polyorganonitriles essentially devoid of backbone carbon-chlorine sites is the primary goal. To satisfy this goal a prerequisite objective entails the preparation of a reactive triazine monomer(s) which can be successfully polymerized, and quantitatively derivatized without significant molecular weight degradation. To accomplish this objective a study of potential catalysts and polymerization reaction conditions which could afford satisfactory yields of high molecular weight polymer was initiated.

3.0 SUMMARY OF WORK

A variety of triazine monomers and catalysts have been screened. Brief highlights of these studies follow:

- (1) Attempts to polymerize $(\text{ClCN})_n$, catalytically in solution or with radiation in the solid state were unsuccessful.

- (2) Attempted polymerization of novel bromo-chloro-s-triazine mixture in organic solvent led, at best, to low yields of product with very low solution viscosity. Attempted polymerization in antimony trihalide solvent led to an apparent reaction, but the product does not appear to be polymeric.
- (3) Attempted polymerization of novel chloro-trifluoroethoxy-s-triazines led to major degradation with nucleophilic catalysts. Tris(trifluoroethoxy)-s-triazine is relatively inert to nucleophiles but isomerizes when heated with certain acidic reagents. The chloro-trifluoroethoxy-triazine monomers were readily prepared in good yield by reaction of lithium trifluoroethoxide with $(ClCN)_3$.
- (4) 2,4-Dichloro-6-phenyl-s-triazine did not polymerize with either acidic or basic catalysts.
- (5) Preparation of the potential monomer trifluoroethyl cyanate has been investigated. A nonvolatile fraction is simultaneously produced which may contain low molecular weight polymer.

4.0 RESULTS AND DISCUSSION

The polymerization of cyanuric chloride, $(ClCN)_3$, was studied first because it is readily available in high purity and is the carbon analog of hexachlorotrichyclophosphazene, $(Cl_2PN)_3$. The phosphazene monomer was successfully polymerized in solution at temperatures below 200°C using a variety of catalysts [Ref. 18].

The polymerization of $(ClCN)_3$ proved unsuccessful and attention shifted to a bromo-chloro-triazine mixture. Replacement of at least one Cl by Br was hoped to be beneficial with respect to boiling point elevation, thus permitting higher reaction temperatures at atmospheric pressure, and to ease of polymerization. The latter effect would be anticipated in light of the greater ease of polymerization of $(Br_2PN)_3$ compared to $(Cl_2PN)_3$ [Ref. 19].

Partially substituted higher boiling mono- or di-chloro-triazine derivatives were investigated as alternate monomers to trihalotriazines for the production of polynitriles. The substituted triazines included 2,4-dichloro-6-phenyl-s-triazine and mono- and bis-(trifluoroethoxy)-chloro-s-triazines. This selection was based on the assumption that the desired ring opening polymerization would be mechanistically similar to the polymerization of $(Cl_2PN)_3$ [Ref. 20].

Phenyl and trifluoroethoxy substituents might be expected to stabilize a $-C=N-$ site and thus facilitate polymerization.

The great majority of polymerizations were carried out under nitrogen at atmospheric pressure, using oil bath temperatures of 220-245°C, and reaction times of 1-3 days. Concentration of catalyst varied from 0.5 to 3% by weight on triazine(s). The solvent generally consisted of 1,2,3,4-tetrachlorobenzene/dichlorobenzene (4 w/l w) and was equal in weight to the monomer charge. The dichlorobenzene (ortho or meta) was employed to eliminate or greatly subdue sublimation of trihalotriazine material. Product was isolated by extraction of solvent(s) and unreacted triazines with dioxane and/or benzene followed by vacuum drying.

4.1 Attempted Polymerization of Cyanuric Chloride

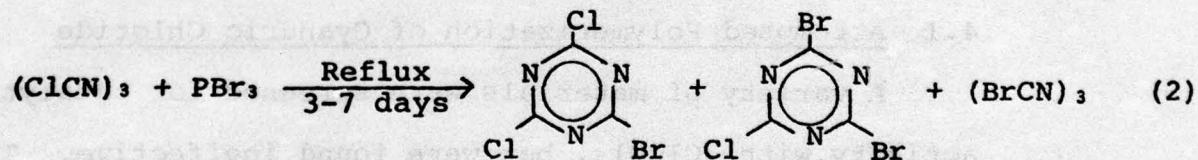
A variety of materials were screened for catalytic activity with $(ClCN)_3$, but were found ineffective. These materials included mercuric methanesulfonate, $(CH_3SO_3Hg)_2O$ [by elemental analysis], $TiCl_4$, KBF_4 , and CH_3SO_3H . These compounds are active catalysts for the polymerization of $(Cl_2PN)_3$ [Ref. 18]. The mixed catalyst $CF_3SO_3Na/4\text{-phenylpyridine}$ led to isolation of blackish solid in low yield, but this material showed no solution viscosity. The above

polymerization attempts were characterized by low reaction temperatures, 205-208°C, because of the relatively low boiling point (190°C) of $(\text{ClCN})_3$.

Attempted preparation of $[\text{ClCN}]_n$ using Co^{60} irradiation was unsuccessful. Vacuum sealed Pyrex tubes containing 5-25 g $(\text{ClCN})_3$ were irradiated at room temperature with up to 7.5×10^5 rads gamma-rays. No polymer was produced. This is in contrast to previous findings by other workers [Ref. 3].

4.2 Attempted Polymerization of Bromo-Chloro-Triazine Mixture

The bromo-chloro-triazine mixtures employed in this program were prepared by the reaction of $(\text{ClCN})_3$ with excess phosphorus tribromide as shown in Equation (2). Such a mixture would be produced commercially by the copolymerization of cyanogen bromide with cyanogen chloride.



The resulting bromo-chloro-triazine mixture was purified by sublimation and based upon gas chromatographic analysis gave a representative molar composition as follows: $(\text{ClCN})_3$ (18%), mono-Br (52%), di-Br (27%), tri-Br (3%). The concentration of di- and tri-bromo components was increased by retreatment with PBr_3 , or by selective removal of $(\text{ClCN})_3$ and mono-bromo material by extraction with benzene. In this manner the concentration of dibromo component was increased to about 50 mole %.

The choice of solvent for the attempted polymerization of bromo-chloro-triazine mixture was critical. Initial studies with 3-chloro-nitrobenzene or diphenyl sulfone readily led to bromine formation. Therefore the relatively hydrogen free 1,2,3,4-tetrachlorobenzene (b.p. 254°C, m.p. 47.5°C) was chosen as solvent. The minor solvent, to control monomer sublimation, initially was o-dichlorobenzene. Gas chromatographic studies indicated that under reaction conditions the o-dichlorobenzene isomerized to the meta isomer. Therefore, m-dichlorobenzene was standardized as the minor solvent.

Weakly basic nucleophilic materials were screened as polymerization catalysts for bromo-chloro-triazine mixture (approximate mole ratio Br:2Br:3Br = 1:2:1) using 1,2,3,4-tetrachlorobenzene/m-dichlorobenzene (4w/lw) solvent. Pyridine (0.5%), 4-phenyl pyridine (1%), or triphenylphosphorus (1.5%) afforded 10-25% yields of dark solid product. The products were insoluble in benzene and dioxane, largely soluble in N-methylpyrrolidinone, and had relative viscosities of 1.02-1.04 (uncorrected; 0.1 g/10 ml N-methylpyrrolidinone, 31°C). The most promising result was obtained with pyridine as catalyst. A 25% yield of product resulted which had a relative viscosity of 1.04 (uncorrected for 29% insolubles). Elemental analysis indicated Br/Cl mole ratio of about two.

Silver trifluoromethanesulfonate and diethylaluminum chloride were also screened for catalytic activity, but were ineffective. The aluminum compound led to generation of significant volatiles.

The manner in which the catalyst was added appeared to have an effect on the reaction. Pyridine or 4-phenylpyridine was either added as a dilute solution to monomer at room temperature or to the solvent monomer mixture at $>180^{\circ}\text{C}$. A higher product yield resulted when the catalyst was added hot.

Attempted polymerizations with bromo-chloro-triazines were characterized by either monomer and/or solvent sublimation or significant side reaction with the hydrogen containing dichloroaromatics. Gas chromatographic analysis and chemical (KOH) trapping showed that the minor solvent m-dichlorobenzene largely reacted under polymerization conditions within two days, presumably with evolution of hydrogen halide. Replacement of m-dichlorobenzene by hexachlorobutadiene or hexachloropropylene led to bromine formation. Use of hydrogen-free pentachloropyridine as major solvent, with pentachloroethane as minor solvent, led to significant volatiles as well as consumption of both solvents during attempted polymerization.

Attempted sealed tube polymerizations at 220-260 $^{\circ}\text{C}$ (oven or sand bath) with standard bromo-triazine mixture or with a

polybromo-rich triazine mixture using a pyridine type catalyst, both with or without tetrachlorobenzene solvent, gave low yields of dark solids with very low relative viscosities. These results were less successful than solvent based polymerization attempts.

An attempt to completely avoid the presence of solvent C-H sites appeared worthwhile to pursue. This would eliminate possible bromine formation and halogenation and/or halogen exchange of solvent by the monomer mixture. Antimony chloride (m.p. 73°C, b.p. 223°C) and bromide (m.p. 97°C, b.p. 280°C) were chosen as replacement solvents. These molten halides should function as solvent and could conceivably have a catalytic polymerization effect. Reactions were conducted 20-68 hours in oil baths at 230-235°C using minor amounts of PBr₃ or POBr₃ for sublimation control. Product yield varied greatly, i.e., from 4 to 90%. Polymer is unlikely since no solution viscosity of product was observed. However, in two instances, SbCl₃-POBr₃, and SbBr₃-PBr₃, combinations, an obvious large increase in reaction viscosity was observed. This may be due to the occurrence of some inorganic reaction. To check this hypothesis the mixture resulting from heating the bromo-chloro-triazine mixture in SbBr₃-PBr₃, was dispersed in N-methylpyrrolidinone and reacted with sodium trifluoroethoxide. If the desired polyhalonitrile was present, it

should be converted to the polyorganonitrile, $-\text{C}=\text{N}-\text{OCH}_2\text{CF}_3$

This was not so since elemental analysis of the product indicated an inorganic composition.

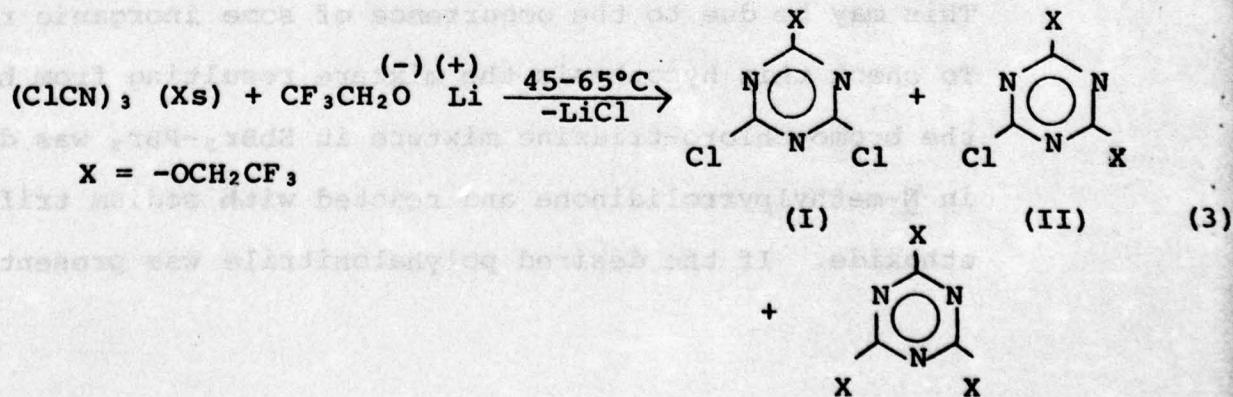
Further studies of a polybromo-triazine rich mixture appear to be indicated. Polymerizations will be attempted in solution at atmospheric pressure using stabler solvents.

4.3 Attempted Polymerization of 2,4-Dichloro-6-Phenyl-s-Triazine

The high boiling 2,4-dichloro-6-phenyl-s-triazine is available in high purity from BASF (Germany). Its polymerizability was studied in bulk using acidic and basic catalysts. Neither the highly acidic $\text{CF}_3\text{SO}_3\text{H}$ (3%) or basic 4-phenyl-pyridine (1%) failed to induce any reaction after 42-48 hours at 235°C . The reactions were monitored by gas chromatography.

4.4 Attempted Polymerization of 2,4-Dichloro-6-Trifluoroethoxy-s-Triazine (I) and 2-Chloro-4,6-Bis(trifluoroethoxy)-s-Triazine (II)

The chloro-trifluoroethoxy-s-triazines (I, II) were prepared by reaction of lithium trifluoroethoxide with cyanuric chloride as shown in Equation (3).



Depending on the concentration of lithium trifluoroethoxide (I) or (II) was the predominant component which subsequently could be purified by distillation. Elemental analysis confirmed the identity of (I).

Attempted bulk polymerizations of (I) and (II) were made using nucleophilic and onium salt catalysts at about 220-225°C. When triphenylphosphorus (0.4%) and particularly 4-phenylpyridine (0.07%) were employed as catalysts significant amounts of highly volatile materials were produced. These volatiles were dry ice and KOH trapped. Compound (I) gave two major volatile components, one boiling below 0°C and one boiling between 0-25°C. Infrared spectrum were consistent with fluorine-containing carbonyl compounds. Interestingly, gas chromatographic analysis showed formation of $(ClCN)_3$ when 4-phenylpyridine (0.07%) was employed. The $(ClCN)_3$ sublimed out and was easily identified. On the other hand, compound (II) predominantly yielded the volatile fraction b.p. >0° to <25°C with little or no formation of $(ClCN)_3$. The nonvolatile products from the reactions of (I) and (III) were very low in molecular weight (relative viscosities 1.00-1.02).

The apparent formation of $(ClCN)_3$ and not of 2,4,6-tris(trifluoroethoxy)-s-triazine from (I) suggests that a detrimmerization and recombination probably takes place. The fate of any formed CF_3CH_2OCN , a thermally unstable compound, is as yet unknown.

In an attempt to moderate the activity of the 4-phenyl-pyridine catalyst sodium trifluoromethanesulfonate (3%) was added as a cocatalyst. This salt completely inhibited the reaction until the 4-phenylpyridine level was greatly increased (from 0.07% to 1.6%). Even then a slow reaction was observed which afforded a lower amount of volatiles per unit conversion. Other additives, NaF (20%) and KPF₆ (3%), also were tested in conjunction with 4-phenylpyridine (0.35-1.5%), but rapid fragmentation occurred. These materials were selected on the basis that the anion would be a considerably poorer nucleophile than chloride.

Halide ion-free onium catalysts tested were $\text{O}_3\text{PCH}_3^{\oplus}\text{CF}_3\text{SO}_3^{\ominus}$ (4.4%) and $\text{O}-\text{C}_6\text{H}_4^{\oplus}\text{NCH}_3^{\ominus}\text{OSO}_3^{\ominus}$ (0.8%) which were relatively inactive or led to fragmentation, respectively. The $\text{O}-\text{C}_6\text{H}_4^{\oplus}\text{NCH}_3^{\ominus}\text{CF}_3\text{SO}_3^{\ominus}$ (3.5%) catalyst showed little fragmentation at about 25% conversion after 7 hours, but noticeable fragmentation after 23 hours.

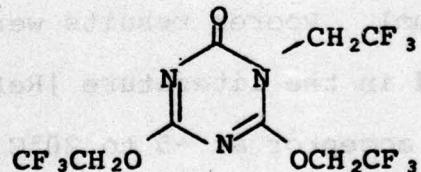
Fragmentation is not believed to be due to thermal activation alone and probably requires the presence of labile chloride. Results with model experiments support the non-thermal hypothesis. Compound (I) gave no reaction when heated in the absence of catalyst and the chlorine-free 2,4,6-tris(trifluoroethoxy)-s-triazine gave no reaction upon heating with

(II) 4-phenylpyridine (0.07%) (232°C, 12.5 hours) or with tri-phenylphosphorus (0.4%) (235°C, 22 hours). One possible explanation for the cleavage reaction is that Cl[⊖] formed by displacement with catalyst acts as a nucleophile at elevated temperature. This could be tested by employing an ionic metal chloride catalyst, but the effort did not appear to be justifiable.

One attempt was made to induce polymerization with a strong Lewis acid. Heating the bis(trifluoroethoxy) derivative with SbCl₅ (3%) led to no reaction.

Attempts to produce an active C[⊕] triazine site for polymerization by use of CF₃SO₃H (3%) as catalyst with tris(trifluoroethoxy) triazine led to no cleavage but essentially quantitative rearrangement. The product was assigned

the structure



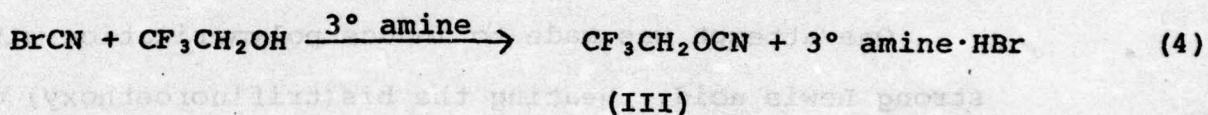
based upon infrared spectrum, gas chromatographic retention time and excellent elemental analysis. A similar, but slightly slower rearrangement, was observed when the quaternary salt

Ø-NCH₃, CF₃SO₃[⊖] was employed as catalyst.

In conclusion, the results with compounds (I) and (II) dictate termination of polymerization studies of fluoroalkoxy substituted triazines.

4.5 Preparation of Trifluoroethyl Cyanate

The preparation of known trifluoroethyl cyanate (III) has been unexpectedly poor via the reaction shown in Equation (4).



The cyanate (III) is desired as an intermediate for the direct preparation of $\text{---C}(\text{OCH}_2\text{CF}_3)=\text{N---}_n$ polymer.

Triethylamine acid acceptor in tetrahydrofuran at 0-25°C gave less than 10% of crude distillable product (b.p. 55°/5 mm; lit. b.p. 32°/2 mm). Poorer results were obtained when acetone, the solvent cited in the literature [Ref. 21], was employed. Pyridine as acid acceptor at -5 to 20°C in methylene chloride gave no distillable product. Fractionation of the distillate residue afforded a trace amount (0.5% yield) of red powder which did not melt to 400°C and which gave a relative solution viscosity of 1.20. Structure assignment was not possible based upon elemental analysis (C, 47.5%; H, 3.4%, F, 23.8%; Br, 7.6%). Lastly, triethylamine was employed in methylene chloride. A large amount of nonvolatile product remained

after vacuum removal of a crude $\text{CF}_3\text{CH}_2\text{OCN}$ fraction (10% yield). The nonvolatile fraction showed some viscosity and is being further characterized to determine if polymeric material is present.

The preparation of trifluoroethyl cyanate will be pursued. Efforts to minimize side reactions will be investigated.

5.0 RECOMMENDATIONS

Two areas appear to warrant further study, namely polymerization of bromo-chloro-triazine mixture and a polymerization study of trifluoroethyl cyanate and characterization of the nonvolatiles produced in attempted preparation of this cyanate material.

The data obtained with the dibromo-triazine rich mixture definitely suggests that a low molecular weight polymer can be obtained in low yield. The presence of -CH containing solvent leads to side reactions and is almost certain to have an adverse affect on the polymerization. Such sites should be eliminated or at least greatly reduced. Pentachlorobenzene (m.p. 86°C, b.p. 277°C) will replace the previously employed 1,2,3,4-tetrachlorobenzene (m.p. 48°C, b.p. 254°C) and will be employed with one of the following minor solvents, 1,3,5-trichlorobenzene (b.p. 208°C), PBr_3 (b.p. 173°C), or POBr_3 .

(b.p. 193°C), which replace the previously used m-dichlorobenzene (b.p. 172°C). The hydrogen free hexachlorobenzene is very high melting (227°C) and would present serious sampling problems. Therefore, it will not be studied.

The pyridine catalyst does have -CH sites, but these should be resistant to attack. The rationale being that pyridine would quaternize to afford a pyridinium complex. This specie should be highly resistant to electrophilic attack by a halotriazine, witness the great difficulty in nitrating or sulfonating pyridinium salts. However, heterocycles such as pyrazine and pyrimidine will be considered for study.

Polymer produced from bromo-chloro-triazine mixture will be reacted with $\text{CF}_3\text{CH}_2\text{ONa}$ in an attempt to prepare $[\text{CF}_3\text{CH}_2\text{OCN}]_n$ homopolymer. This product(s) will be characterized for solution viscosity, physical properties, and elemental analysis.

The preparation of trifluoroethyl cyanate is expected to be improved by using milder reaction conditions. Lower reaction temperatures and/or the use of sodium trifluoroethoxide reagent will be studied. Trifluoroethyl cyanate will be screened for polymerization activity primarily with nucleophilic catalysts. The catalyst and/or solvent will be varied so as to minimize cyclic trimerization.

6.0 EXPERIMENTAL

6.1 Preparation of Bromo-Chloro-Triazine Mixture

A 2-liter 3-neck flask was charged with PBr_3 (400 ml, 1.14 kg) and cyanuric chloride (300 g), which was stirred and refluxed for 1 week (final temperature = $163^\circ C$). Excess PBr_3 was removed by distillation until the reaction liquid reached $190^\circ C$. Chlorobenzene (400 ml) was added slowly at reflux. Heptane (300 ml) was added and the mixture was refluxed for 2 hours. The reaction was cooled to about $-20^\circ C$ and precipitated solids were filtered and washed with fresh heptane-chlorobenzene (150 ml, 2v/lv). The solid was vacuum dried briefly and sublimed at 1.6 mm Hg pressure in an oil bath at $140-182^\circ C$. After discarding the initial sublimate (27 g) the major product fraction (209 g) was collected. The product was ground under nitrogen in the dry box and elemental analysis and vapor phase-liquid chromatography were obtained. Found: C, 15.6%; H, 0.2%; Cl, 31.0%; Br, 35.1%. Calculated for $C_3BrCl_2N_3$: C, 15.7%; H, 0.0%; Cl, 31.0%; Br, 35.0%. Gas chromatographic analysis indicated a predominance of 2-bromo-4,6-dichloro-s-triazine with lesser amounts of cyanuric chloride and 2,4-dibromo-6-chloro-s-triazine and a very small amount of cyanuric bromide. The bromine concentration of the bromo-chloro-triazine mixture was

further increased by either resubjecting the mixture to several days reflux with PBr₃, or by extraction with benzene (1/2 liter per 100 g mixture).

6.2 Attempted Polymerization of Bromo-Chloro-Triazine Mixture-Polychlorobenzene Solvent

Under nitrogen a dry flask was charged with 1,2,3,4-tetrachlorobenzene (4.0 g), m-dichlorobenzene (1.0 g), bromo-chloro-triazine mixture (5.0 g) (25%, 50%, 25 mole % for mono-, di- and tri-bromo components) and pyridine (25 mg) in hexane (2 ml). The hexane was removed under vacuum and the flask immersed in an oil bath at 230-234°C. After 67 hours the weight gain of a KOH tube, which was attached to the flask through an intermediary dry ice trap, was 0.224 g. Gas chromatographic analysis of the reaction showed an approximate two-thirds decrease in m-dichlorobenzene and little reduction in triazine components. Product was isolated by washing the reaction mixture twice with benzene (20 ml) and once with benzene-dioxane (20 ml, 1v/lv). High vacuum drying 3 hours at 140°C afforded 1.1 g of blackish solid. This material did not melt up to 360°C. The relative viscosity was 1.04 (0.1 g/10 ml N-methylpyrrolidinone, 31°C) (uncorrected for 29% insolubles).

Elemental analysis calculated for C₃Br₂ClN₃: C, 13.2%; Br, 58.5%; Cl, 13.0%. Found: C, 16.4%; H, 0.8%; Br, 54.7%; Cl, 13.1%. The presence of hydrogen cannot be explained at this time.

The effects of catalyst and solvent in the attempted polymerizations of bromo-chloro-triazine mixture are shown in Table I.

6.3 Attempted Polymerization of Bromo-Chloro-Triazine Mixture-SbBr₃, Solvent:Derivatization with CF₃CH₂ONa

Under nitrogen a dry flask was charged with bromo-chloro-triazine mixture (5.0 g) (25%, 50%, 25 mole % of mono-, di- and tri-bromo components) and SbBr₃ (10 g). The flask which was fitted with a condenser was placed in an oil bath at 230°C and PBr₃ (1 g) added. The reaction was heated for 20 hours at which time it was an almost immobile very dark mass. The contents were triturated several times with dioxane (30-35 ml), several times with dioxane containing 5% N-methyl-pyrrolidinone (5 ml). The product was precipitated by addition of dioxane (30 ml). This solution-precipitation process was repeated again. The resultant gummy precipitate did not change in texture after it was washed with dioxane. However, washing with trifluoroethanol (35 ml) converted the gum to a pinkish solid which was vacuum dried two hours at 140°C to afford 4.6 g solid. This material showed no solution viscosity. Infrared (Nujol) spectrum showed no distinctive absorptions.

The above experiment was repeated except that the reaction contents were largely dissolved directly in N-methyl-pyrrolidinone (30 ml). To this mixture was added, over 3/4

TABLE I

Attempted Polymerizations^a of Bromo-Chloro-Triazine Mixture^b

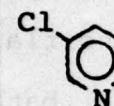
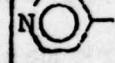
Run	Catalyst (%)	Oil Bath		Yield (%)	$[\eta]_{\text{rel}}^{\text{c}}$	Remarks ^d
		Temp./Hours	(°C)			
1	$\text{CF}_3\text{SO}_3\text{Ag}$ (3)	230/40		-	-	Increase in $(\text{ClCN})_3$ and decrease in di-Br component
2	 (10) (minor solvent)	230/3		-	-	Extensive sublimation
3	 (1)	225/47		-	-	 as solvent; significant drop in solvents
4	 (0.5)	235/20		13 (rust)	1.02	 CF_3 as minor solvent; significant drop in solvents
5	$(\text{C}_2\text{H}_5)_2\text{AlCl}$ (1.2)	235/48		-	-	Extensive forma- tion of volatile acid
6	 (0.5)	234/67		22 (black)	1.04 (uncorr. for 29% in- soluble)	Large decrease in $\text{C}_6\text{H}_4\text{Cl}_2$
7	 (0.5)	230-35/54		3 (black)	1.02	$\text{C}_6\text{H}_2\text{Cl}_4$ sole solvent
8	 (1) (added hot)	235/40		20 (dark rust)	1.03	All components except $(\text{ClCN})_3$, show decrease

TABLE I (continued)

Run	Catalyst (%)	Oil Bath Temp./Hours (°C)	Yield (%)	[n] _{rel} ^c	Remarks d
9	 (1) (added cold)	235/44	10 (brown)	1.03	
10	 (0.9) (added cold)	256-60/66 (sealed tube)	~3	1.00	
11	 (0.5)	203-07/49	5	1.04	Cl ₂ C=CCl ₂ as minor solvent (20%)
12	 (0.5) (added hot)	245/48	2 (brown)	1.00	
13	 (0.5) (added hot)	245/1/4	-	-	(4-ClC ₆ H ₄) ₂ SO ₂ as major solvent rapid generation of Br ₂
14	Ø ₃ P (1.5)	245/46	12	1.02 (brick red)	

a Unless stated otherwise equal weights of monomer and solvent were employed; the solvents consisted of 1,2,3,4-tetrachlorobenzene (80%) m-dichlorobenzene (20%)

b Runs 1-6 utilized mono-bromo-triazine rich mixture, Runs 7-14 utilized dibromo triazine rich mixture

c Concentration of 0.10 g sample per 10 ml N-methylpyrrolidinone, 31°C

d Solvent and monomer components monitored by gas chromatographic analysis

hour at ice temperature, sodium trifluoroethoxide which was prepared from sodium (6.19 g, 0.27 mol), trifluoroethanol (29.7 g, 0.297 mol), and tetrahydrofuran (60 ml). The temperature was gradually raised to room temperature and maintained for 2 days. The reaction was treated with 10% aqueous HCl (150 ml), solids suction filtered off, solids washed twice with distilled water (150 ml), once with acetone (100 ml), and vacuum dried at 50°C for 2 hours. The resulting brown solid showed no solution viscosity, gave a positive Beilstein test and did not melt up to 400°C. Elemental analysis confirmed the material to be largely inorganic. Found: C, 3.0%; H, 0.5%; Br, 0.8%; Ash, 86.8%.

6.4 Preparation of 2,4-Dichloro-6-Trifluoroethoxy-s-Triazine

A 3 liter flask was charged with 500 ml each of dioxane and methylene chloride, cyanuric chloride (718 g, 3.9 moles), and MgO (5 g). The reaction was stirred overnight at room temperature under nitrogen and heated to 50°C at which time a lithium trifluoroethoxide mixture [prepared by refluxing overnight 300 ml trifluoroethanol and 36 g (1.5 moles) anhydrous LiOH] diluted with dioxane (100 ml) was gradually added. Reflux was maintained at 63-65°C for 2 hours and the reaction mixture was cooled to ice temperature, diluted with methylene chloride (100 ml), and washed thrice with 3 liters of cold 10% HCl. The precipitated excess (ClCN)₃ was filtered, and the extract in the organic layer was dried over CaCl₂. The

bulk of CH_2Cl_2 was removed by distillation whereupon heptane (100 ml) was added and the stripping continued until the residue reached 130°C. Product was vacuum distilled with the following results:

Fraction	B. P. at 12 mm Hg (°C)	Yield (g)	Comp. by Gas Chrom. Number of $\text{CF}_3\text{CH}_2\text{O}$ - groups/mol.		
			0	1	2
I (forerun)	105-106	21			
II	106-109	100	1.5	90	8.5
III	109-114	67	0	84	16
IV	73-95 (0.6 mm)	37	0	20	80

Elemental analysis of Fraction II was: C, 24.1%; H, 0.7%; Cl, 30.2%. Theory for $\text{C}_5\text{H}_2\text{Cl}_2\text{N}_3\text{O}$: C, 24.2%; H, 0.8%; Cl, 28.6%. Redistillation of Fraction II gave 94% purity material with b.p. 117-119°/26 mm.

Doubling the lithium trifluoroethoxide led to the formation of 2-chloro-4,6-di(trifluoroethoxy)-s-triazine as the major product, b.p. 131-133.5°C/25 mm. The distilled product was contaminated with about 3% of monotrifluoroethoxy derivative and 1% of 2,4,6-tris(trifluoroethoxy)-s-triazine.

6.5 Attempted Polymerization of 2,4-Dichloro-6-Trifluoroethoxy-s-Triazine

Under nitrogen 2,4-dichloro-6-trifluoroethoxy-s-triazine (15 g) was added to a dry flask, fitted with a condenser, and

which was attached to a trap immersed in dry ice which in turn was connected to KOH tube to the nitrogen manifold. The flask was lowered into a 223°C oil bath and when the inside liquid was 170°C 4-phenylpyridine (0.050 g) was added as a 30% benzene solution. After 1.5 hours an appreciable amount (ca. 0.2 g) of white crystalline sublimate had formed on the condenser joint. This sublimate was later shown to be cyanuric chloride. Gas chromatographic analysis indicated 61% conversion of starting material after 3.5 hours at about 211°C. Approximately 4-5 ml of liquid had been dry ice trapped whereas the KOH trap showed a gain of 6 mg. Total weight of gaseous product was ca. 5.5 g. The trapped volatiles were placed in an ice water bath. The low boiling material which boiled off was collected in cold chloroform. Infrared spectrum of fractions b.p. <0°C and b.p. >0°C to <25°C were taken and were indicative of C-F containing materials. The hard solidified brown solid (8.3 g) in the reaction flask was not characterized.

6.6 Attempted Polymerization of 2,4,6-Tris(trifluoroethoxy)-s-Triazine

Under nitrogen 2,4,6-tris(trifluoroethoxy)-s-triazine (10 g; m.p. 55-57°C) was added to a dry flask. The triazine was melted and, with stirring, a solution of trifluoromethane-sulfonic acid (0.3 g) in 1,1,2-trichloro-1,2,2-trifluoroethane

(Freon TF) (1.2 g) was added. The flask was attached to a nitrogen manifold through a dry ice trap and a KOH trap, and immersed in an oil bath at 220°C. The Freon TF was allowed to vaporize out and the bath raised to 240°C. Gas chromatographic analysis of starting material after 5 and 20 hours showed 25 and 90% conversion, respectively. A slightly higher boiling component appeared to form quantitatively. Approximately 0.3 ml clear colorless liquid was collected in the dry ice trap, whereas the KOH trap gained 16.5 mg. The dark viscous liquid product in the flask was triturated twice with heptane-benzene (12 ml, 3v/lv) and then twice recrystallized from benzene (50 ml) to give white crystalline solid, m.p. 93-94°C. Infrared analysis showed strong absorptions at 5.88, 6.19, 6.82, 6.95, 7.06 (doublet), and 7.77, 8.00 (doublet) microns and moderate absorptions at 5.60, 7.44, 8.12, 8.25 (doublet), 9.22, 9.80, 10.51, 12.1 and 12.7 microns. Analysis calculated for $(CF_3CH_2O)_3C_3N_3$: C, 28.8%; H, 1.7%; N, 11.2%. Found: C, 28.9%; H, 1.6%; N, 11.2%. The product is postulated as the isomer of starting material in which one, possibly two, $-CH_2CF_3$ group has rearranged to a nitrogen atom.

6.7 Attempted Preparation of Trifluoroethyl Cyanate

Under nitrogen with stirring, trifluoroethanol (29.8 g, 0.298 mol) was added to a solution (0°C) of cyanogen bromide (33.2 g, 0.313 mol) in methylene chloride (100 ml), followed

by triethylamine (30.1 g, 0.298 mol) over a 45 minute period while maintaining the reaction temperature at 0-5°C. Stirring was continued six hours at ice temperature and 24 hours at room temperature. The reaction was stirred well with pentane (100 ml) and then suction filtered to remove precipitated amine hydrobromide which was washed with methylene chloride/pentane (50 ml, 1v/1v). The solvents from the filtrate were removed at room temperature under house vacuum to give a mixture of reddish liquor and some white solid. This mixture was flash distilled at 25°C/0.25 mm to give a nonvolatile water soluble residue and a clear distillate (10 g) which was then redistilled at 55°C/2 mm to give 8.4 g liquid. Gas chromatographic analysis showed the presence of significant solvent. Redistillation through a short (6") Vigreux column gave 3.6 g liquid, b.p. 35°C/4 mm. Based on boiling point it was anticipated that this material would be trifluoroethyl cyanate. However, the characteristic $-\text{OC}\equiv\text{N}$ infrared absorption at about 4.5μ was not present.

The water soluble residue from the first distillation was dissolved in methylene chloride (50 ml), washed twice with water (50 ml), stripped of solvent, and vacuum dried at 60°C for 4 hours to give a red gummy material (17.2 g). The relative viscosity was 1.013 (0.1 g/10 ml N-methylpyrrolidinone, 31°C). The material is soluble in benzene, methanol, isopropyl

alcohol, but insoluble in petroleum ether. Fractionation was attempted by dissolving in benzene (30 ml) and precipitating a red gum by addition of petroleum ether (60 ml). Vacuum drying this material at 60°C for six hours afforded a hard gum (6 g) which had very slow cold flow and gave a negative Beilstein test. The relative solution viscosity of this material was 1.03. Elemental analysis: C, 32.0%; H, 2.3%; N, 16.5%; F, 35.3%. Calculated for $[CF_3CH_2OCN]_n$: C, 28.8%; H, 1.7%; N, 11.2%; F, 45.6%.

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